Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Chain-extending of Hydroxytelechelic Polybutadiene: Synthesis and Characterization

Michaël Lemoine[a]; Claire-Helene Brachais[a]; Gilles Boni[a]; Laurent Brachais[b]; Jean-Pierre Couvercelle[a]
[a] Institut de Chimie Moléculaire de l'Université de Bourgogne, Systèmes Hybrides Multifonctionnels, Université de Bourgogne, Dijon, France [b] EMMA, AgroSup, Université de Bourgogne, Dijon, France

To cite this Article Lemoine, Michaël , Brachais, Claire-Helene , Boni, Gilles , Brachais, Laurent and Couvercelle, Jean-Pierre(2011) 'Chain-extending of Hydroxytelechelic Polybutadiene: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 48: 2, 100 — 107

To link to this Article: DOI: 10.1080/10601325.2011.534717

URL: http://dx.doi.org/10.1080/10601325.2011.534717

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2011) **48**, 100–107
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2011.534717

Chain-extending of Hydroxytelechelic Polybutadiene: Synthesis and Characterization

MICHAËL LEMOINE[1], CLAIRE-HELENE BRACHAIS[1,*], GILLES BONI[1], LAURENT BRACHAIS[2], and JEAN-PIERRE COUVERCELLE[1]

[1] *Institut de Chimie Moléculaire de l'Université de Bourgogne, Systèmes Hybrides Multifonctionnels, Université de Bourgogne, UFR Sciences et Techniques, Dijon, France*
[2] *EMMA, AgroSup, Université de Bourgogne, esplanade Erasme, Dijon, France*

Received June 2010, Accepted August 2010

Extension of hydroxytelechelic polybutadiene oligomers ($\overline{\text{Mn}} = 3200$ g/mol) is performed in mild conditions, in order to avoid backbone modifications, using succinic anhydride or methylenedicyclohexyl diisocyanate. The two routes present significative extension of the initial oligomers. Extension through the anhydride route, in the presence of DCC and DMAP, leads to new hydroxytelechelic oligomers ($\overline{\text{Mn}} = 8000$ g/mol). Extension through the diisocyanate route, catalyzed by DBTL at 65°C leads to hydroxytelechelic oligomers of higher average molecular weight ($\overline{\text{Mn}} = 20000$ g/mol). New materials are characterized by FTIR/^{1}H-NMR and changes in their Tg according to $\overline{\text{Mn}}$, are discussed. The influence of reaction time on the length of the macromolecular chains is also studied.

Keywords: HTPB, chain-extented, HMDI, succinic anhydride, glass transition temperature

1 Introduction

Oligomers of hydroxy terminated polybutadiene derive either from the free radical or from the anionic polymerisation of butadiene. Radical polymerization is conducted in an alcoholic medium (isopropanol or ethanol) using H_2O_2 as the initiator in order to generate more than two hydroxyl extremities ($f_{OH} = 2.5$) (1–4). Anionic polymerisation (4–7) of butadiene generates pure difonctional material ($f_{OH} = 2.0$) (8). Oligomers of hydroxy terminated polybutadiene (HTPB) are commonly used as propellants in many solid rocket motors (9), as adhesive sealant(10) and as encapsulation resins. HTPB oligomers also present unique properties of hydrolytic and moisture stability, high solvent and chemical resistance and excellent low temperature flexibility. For all these reasons they are valuable candidates for synthesis of polyesters (11), polyurethanes (12–15) poly(urethane-imide)s (16) and poly(urethane-urea) (17, 18). In these materials, HTPB is used as the soft segment and the properties of the resulting copolymers or networks depend on the chain length of the HTPB block. In a previous study we reported the synthesis in mild conditions of polybutadiene-polycaprolactone multi-blocks based on HTPB R45 HT® (19) and ε-caprolactone. In these materials, the composition (and the physical properties) of the resulting triblocks is governed by the amount of polycaprolactone since the HTPB block is invariant. In order to obtain better control over the mechanical properties of such copolymers, chain extending of the HTPB block could be an interesting way of varying the final materials properties. In the literature little work describes the chain extension of these oligomers. Radhakrishnan et al. (6) performed the reactions of various anhydride with HTPB oligomers in order to obtain unsaturated polyester-imide but they did not describe the extended HTPB materials. In 2006, Zheng et al. (20) reported the extension by a factor 1.46 of HTPB starting from oligomers with $\overline{Mv} = 3900$ g/mol. The reaction was conducted in mild conditions using maleic anhydride as the extending agent and led to carboxytelechelic oligomers. We report herein the synthesis of extended HTPB by the anhydride route (reaction with succinic anhydride) and by the diisocyanate route (reaction with methylenedicyclohexyl diisocyanate). Thermal properties of the resulting materials will also be briefly discussed.

2 Experimental

2.1 Materials

Tetrahydrofuran (Aldrich) was distilled on sodium and benzophenone and dried over molecular sieves (4 Å) before

---

*Address correspondence to: Claire-Helene Brachais, Institut de Chimie Moléculaire de l'Université de Bourgogne, Systèmes Hybrides Multifonctionnels, UMR CNRS 5260, Université de Bourgogne, UFR Sciences et Techniques, 9 avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France. Fax +33 (0)3 80 39 60 98; E-mail: claire-helene.brachais@u-bourgogne.fr

use. Hydroxy telechelic polybutadiene (HTPB) G2000® ($\overline{M}n$ = 2000 g/mol (tonometry values), f_{OH} = 2.0) was kindly supplied by Nisso-Soda. Microstructures studies, using the NMR technique, indicate 85% of 1,2 units (vinyl units) and 15% of 1,4 units [21, 22]. HTPB is degassed for 4 h at 80°C under vacuum (10^{-2} mmHg) before use. Succinic anhydride (SA) and 4,4′-methylenebis(cyclohexyl isocyanate) (HMDI) (Aldrich) were used as received. 4-Dimethylaminopyridine (DMAP) was purchased from Fluka with a purity ≥98% and was used as received. A solution of 1 mol/L in dichloromethane of DCC, dicyclohexyldimethylcarbodiimide, (Aldrich) was stocked in a bottle equipped by a sure seal cap.

2.2 Synthesis of Chain-extended HTPB

1.05 g (n_{OH} = $1.05.10^{-3}$ mol) of HTPB were introduced into a 100 mL round bottom flask equipped with a switchable inlet for nitrogen and a vacuum connector. HTPB was first degassed for 4 h under vacuum at 80°C.

Diisocyanate route: 10 mL of dried THF was added followed by 6.3 10^{-1} mg (10^{-6} mol) of the catalyst (DBTL) and 131 mg (n_{NCO} = 10^{-3} mol) of HMDI. The mixture was stirred at room temperature or at 65°C. The reaction was allowed to proceed until complete disappearance of isocyanate functions.

^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm: 0.95–1.29 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB], 1.80–2.16 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB], 2.51[m, *Cy*], 3.32 [m, N-C*H*], 3.69 [m, O*H*], 3.97 [broad s, N*H*], 4,00 [m, CH_2CH_2], 4.74–4.95 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB], 5.19–5.58 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB].

Anhydride route: 10 mL of dried THF was added followed by 1mL (10^{-3} mol) of the DCC solution, 24 mg (2.10^{-4} mol) of DMAP and 50 mg (n_{COOCO} = 5 10^{-4} mol) of succinic anhydride. The mixture was stirred at room temperature, for a maximal reaction time of 24 h, and filtrated to eliminate solid DCU. The polymer solution is then poured in ethanol and centrifuged (three times) at 16000 rpm during 10 min in order to remove the DMAP and the unreacted succinic anhydride.

^{1}H-NMR (300 MHz, $CDCl_3$)δ ppm: 0.94–1.30 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB], 1.78–2.15 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB], 3.65 [m, O*H*], 4,00 [m, CH_2CH_2], 4.74–4.96 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB], 5.19–5.56 [$(CH_2{=}CH)CHCH_2$ in 1,2 structure of PB].

2.3 SEC

SEC analyses were carried out on a Gynkotek P580A apparatus equipped with 2 PolyPore columns from Polymer Laboratories (300*7.5 mm) and a IOTA 2 refractive index detector. Polystyrene standards were used for column calibration. Polymer samples were dissolved in THF (10 mg/mL) and elution was performed at 20°C at a flow rate of 1mL/min, with THF as solvent. Before injection, a small amount of dibutylamine is added to the samples obtained from the isocyanate route, in order to convert the unreacted isocyanate groups to urea groups.

3 Results and Discussion

3.1 Thermal Stability Study of HTPB Oligomers

Before testing the chain-extending parameters of the oligomers, we performed a thermal stability study of HTPB oligomers.

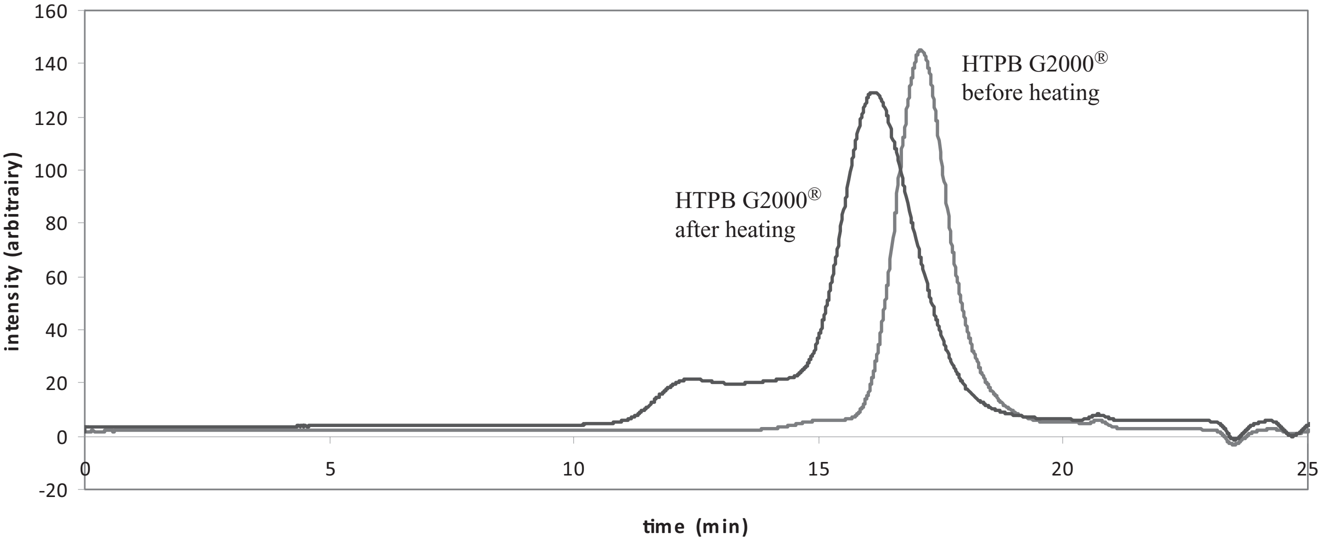

Fig. 1. Size exclusion chromatography analysis of HTPB G 2000® before and after heating at 150°C during 16 h under N_2.

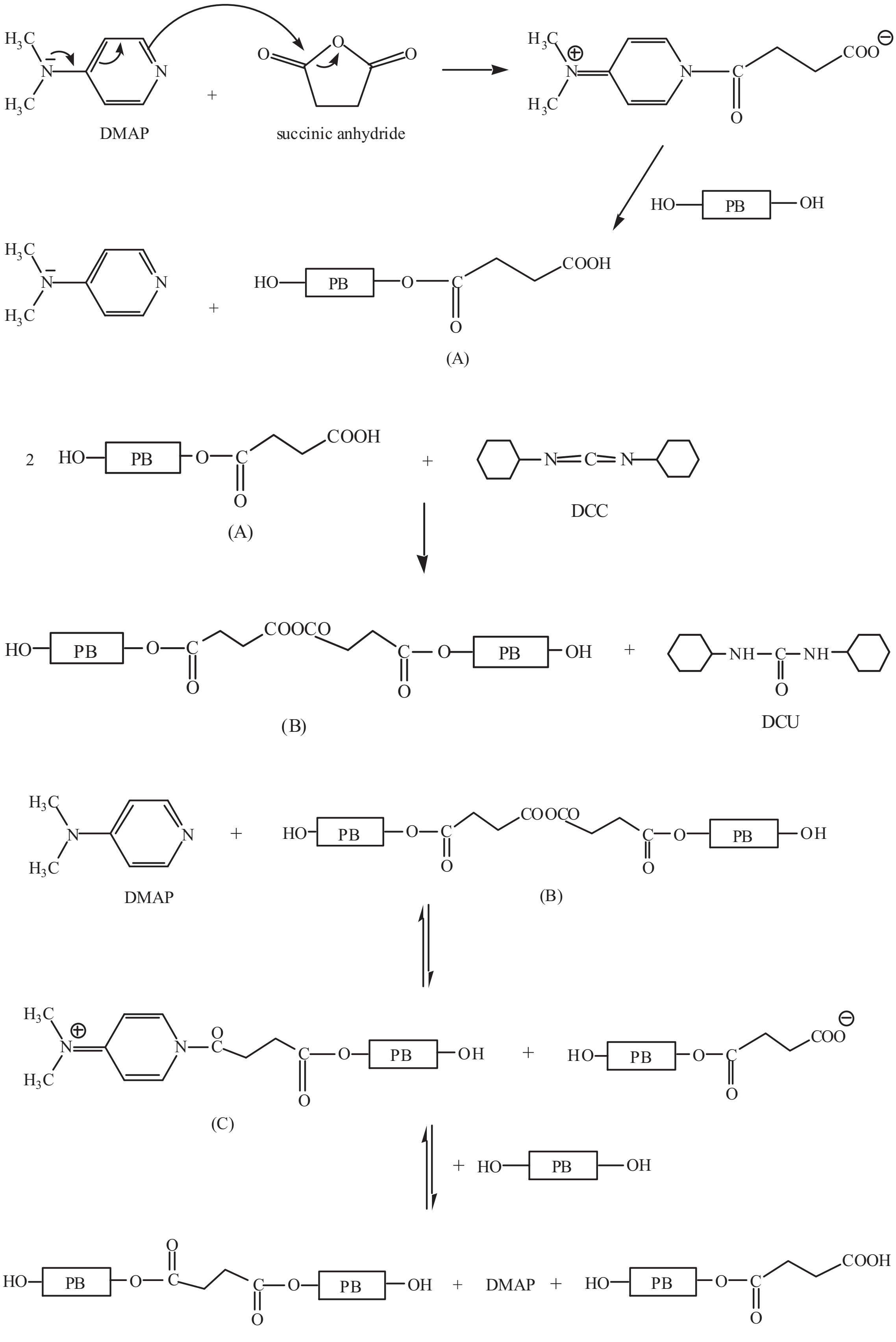

Fig. 2. Proposed mechanism for the diester linkage formation.

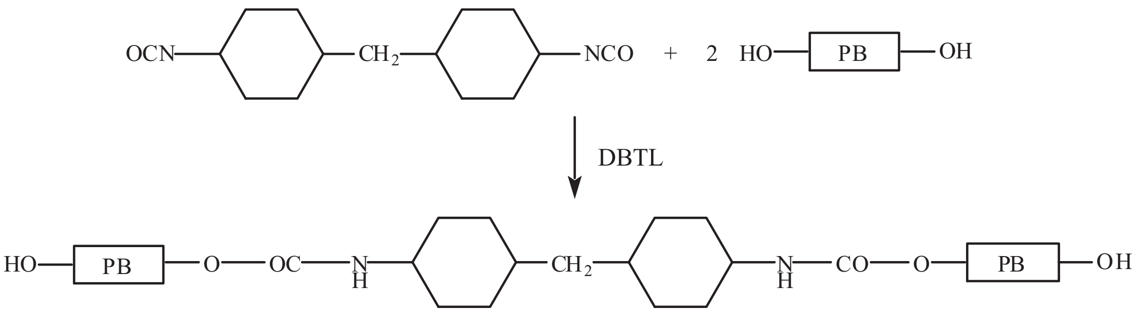

Fig. 3. Mechanism of urethane linkage formation for 2 equivalents of HTPB.

Figure 1 shows SEC chromatograms of starting HTPB G2000® ($\overline{Mn} = 3200$ g/mol, $\overline{Mw} = 5100$ g/mol, equivalent to standard PS) and HTPB after heating at 150°C during 16 h under N_2. In these conditions, although no gelification of the medium is observed, an extension of the oligomers is detected.

This material presents a very high polydispersity index of 6.3 for a quite low extension factor since $\overline{Mn} = 8700$ g/mol and $\overline{Mw} = 54500$ g/mol. This is due to branching reactions occurring already after 16 h. After 24 h, the reaction conditions have led to the crosslinking of HTPB. Indeed, HTPB undergoes chain extension or even crosslinking when heated without any catalyst at 150°C under N_2 or air. Moreover, on a study concerning the aging characteristics of HTPB propellant, Zhang (23) showed that the oxidative ageing of the HTPB could result in the formation of a network at relatively low temperatures (60°C to 80°C). For all these reasons, we focused on a controlled extension of the chains at low temperature and under nitrogen atmosphere. Under these smooth operating conditions i.e., 65°C, 24 h under N_2, no spontaneous extension or crosslinking of the HTPB is detected.

3.2 Chain Extension of HTPB Oligomers

The reaction involves a difonctional molecule which acts as a chemical link between two HTPB oligomers. In this aim, the use of succinic anhydride leads to the formation of an ester linkage (Fig. 2), whereas the reaction with a diisocyanate leads to the formation of a carbamate link (Fig. 3).

In earlier studies, it was observed that DCC promotes esterification of alcohols under mild conditions (24, 25). The proposed mechanism of ester formation is shown in Figure 2. First, succinic anhydride is converted by DMAP to carboxylic acid and linked to a first HTPB moiety (A). (A) reacts with DCC leading to anhydride (B). (B) forms an acyl pyridinium species (C) with the DMAP catalyst. Nucleophilic attack by the hydroxyl group of HTPB on the acyl group of (C) generates the expected ester and DMAP catalyst.

Thus, using DCC/DMAP as a coupling agent/catalyst, extension of the HTPB oligomers is conducted in anhydrous THF at room temperature to avoid any chemical modification of HTPB skeleton. Extended materials were obtained by varying molar ratios (anhydride /HTPB oligomer) from 1:1.05 to 3:4 in order to conserve the hydroxyl extremities of the chains. Figure 4 summarizes the global extension mechanism.

A second way of extension of the HTPB diol was investigated using a diisocyanate. Because of their high reactivity toward diols or diamines, diisocyanates are widely used in the chemistry of polyurethanes elastomers (26, 27). The HTPB oligomers, extended by a urethane linkage (Fig. 3), were prepared by reacting one equivalent of diisocyanate with various equivalents of HTPB (at least 1.05 hydroxyl

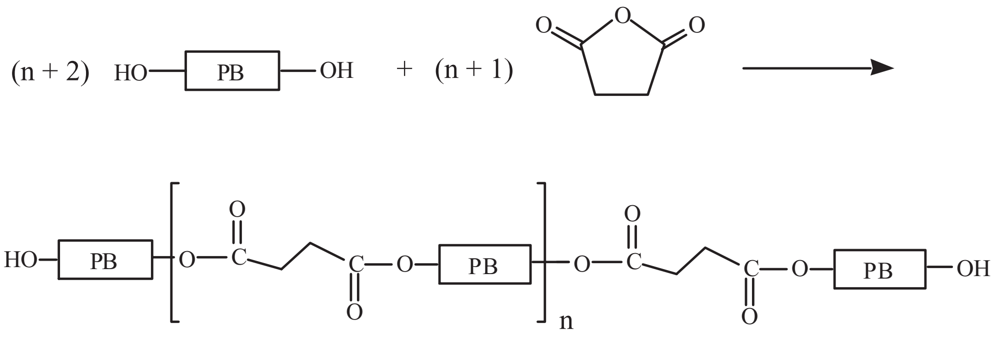

Fig. 4. Summary of the chain extension mechanism by the ester route.

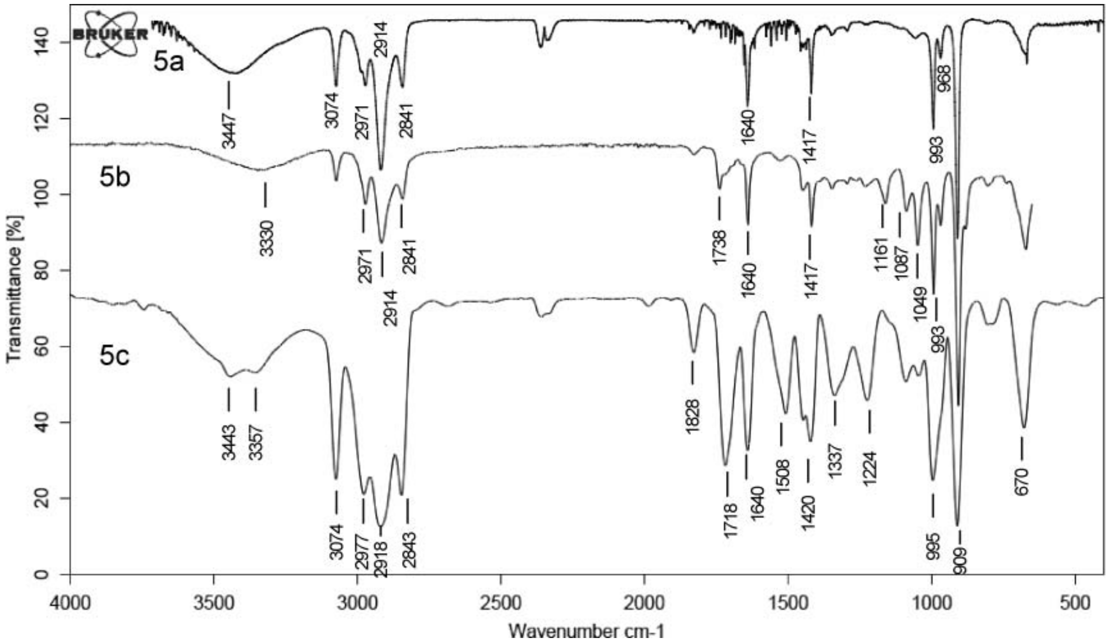

Fig. 5. Infrared analysis of HTPB G2000®(a), anhydride extended HTPB (b) and diisocyanate extended HTPB (c).

equivalent) in order to keep the hydroxyl extremities as described in Figure 3.

3.3 Characterization

The infrared spectra of HTPB G2000®, anhydride extended HTPB and diisocyanate extended HTPB are shown in Figures 5a, b and c, respectively. For all these materials, the presence of hydroxyl extremities is evidenced by the large absorption band in the range 3300–3450 cm^{-1}. On Figure 5a, the band at 3074 cm^{-1} is assigned to $=CH_2$stretching, whereas the bands at 2971, 2914 and 2841 cm^{-1} are assigned to C-H stretching. Another characteristic band detected at 1640 cm^{-1} is assigned to C=C stretching. Delta bands for =CHcould also be detected at 1417 cm^{-1} (in the plane vibration), 993 cm^{-1}, 968 cm^{-1} and 909 cm^{-1} (out of the plane vibration). All these bands are also detected in Figures 5b and c, in addition with specific ester and carbamate bands. Indeed, on Figure 5b, the carbonyl ester absorption band, is detected at 1738 cm^{-1}and the bands at 1161 cm^{-1}, 1087 cm^{-1} and 1049 cm^{-1} correspond to the C-O stretching. On Figure 5c, the carbonyl carbamate absorption band is detected at 1718 cm^{-1}. The second band above 3300 cm^{-1}is assigned to N-H stretching, additionally with the band at 1508 cm^{-1} for N-H$_\delta$. The characteristic bands at 1224 correspond to N-CO-O stretching symmetric.

For each material, ^{1}H-NMR characterization (see Experimental) is in accordance with the chain-extending of the starting oligomers by the two chemical routes. Each ^{1}H NMR spectrum shows the typical chemical shifts for the HTPB skeleton. Moreover, for the anhydride extended polymer, the peak at 4 ppm corresponds to the –OCO-CH_2-CH_2–COO- link between two HTPB blocks. The ^{1}H-NMR spectrum of the diisocyanate extended polymer displays three characteristic resonances for the diisocyanate link : two multiplets at 2.51 ppm and 3.32 ppm for the cyclohexyl protons and the N-CH fragment, respectively and a broad signal at 3.97 ppm for the urethane NH group.

The SEC analysis of the materials allows the quantification of the chains extension. Table 1 compares the average molar mass for the materials based on HTPB and succinic anhydride with DMAP and DCC as catalysts.

Comparison between run 1 and runs 2, 3 or 4 demonstrates that the use of DMAP and DCC is essential to perform the HTPB extension in mild conditions. Indeed, a procedure without catalyst does not allow any extension of the chains (run 1). The use of DMAP and DCC makes possible the extension of the HTPB chains by two (run 1) at

Table 1. Molar ratio of succinic anhydride in equivalent acid/hydroxyl from HTPB and average molar mass of extended HTPB oligomers after 24 h at room temperature Run 1 = Run 4 without DMAP and DCC as catalysts

Run	*Molar ratio (succinic anhydride in equivalent acid/hydroxyl from HTPB)*	$\overline{Mn}$	$\overline{Mw}$	*DPI*
HTPB	0:1	3200	5100	1.6
1	1:1.05	3200	5100	1.6
2	1:2	3400	7500	2.2
3	3:4	4100	8200	2
4	1:1.05	6700	12300	1.8

Table 2. Molar ratio of methylenedicyclohexyl diisocyanate /hydroxyl from HTPB and average molar mass of extended oligomers after 24 h.

Run	*Molar ratio isocyanate /hydroxyl from HTPB*	$\overline{Mn}$ *(g/mol)*	$\overline{Mw}$ *(g/mol)*	*DPI*
HTPB	0:1	3200	5100	1.6
5	1:1.05	9400	16300	1.7
6	1:2	7100	12800	1.8
7	3:4	8200	16200	2
8	1:1.05	19400	54200	2.8

Run 5 = run 8 without tin octoate as a catalyst [DBTL] = 10^{-4} mol/L

room temperature in 24 h. As expected, the highest average molecular weights are obtained for initial stoechiometric conditions (run 4). The fact that the average molecular weight values were rather low can be related to the low reaction temperature (20°C). Higher reaction temperatures should allow one to increase the degree of polymerization (28).

Table 2 compares the average molar mass for the materials based on HTPB and methylenedicyclohexyl diisocyanate with DBTL as catalyst, in anhydrous THF at 65°C during 24 h.

The number average molar masses obtained from SEC (Table 2) are much higher than the molar mass of the starting HTPB. Unlike the precedent reaction, the HTPB extension occurs even without the use of a tin catalyst (run 5). The extension factor without any catalyst is around three (based on $\overline{Mn}$ values) indicating the great intrinsic reactivity of isocyanate functions towards hydroxytelechelic functions of the polybutadiene. However, run 8 shows that the best way to obtain high average molecular weights is to use stoechiometric amounts of isocyanate and hydroxyl functions in the presence of DBTL. The higher the ratio departs

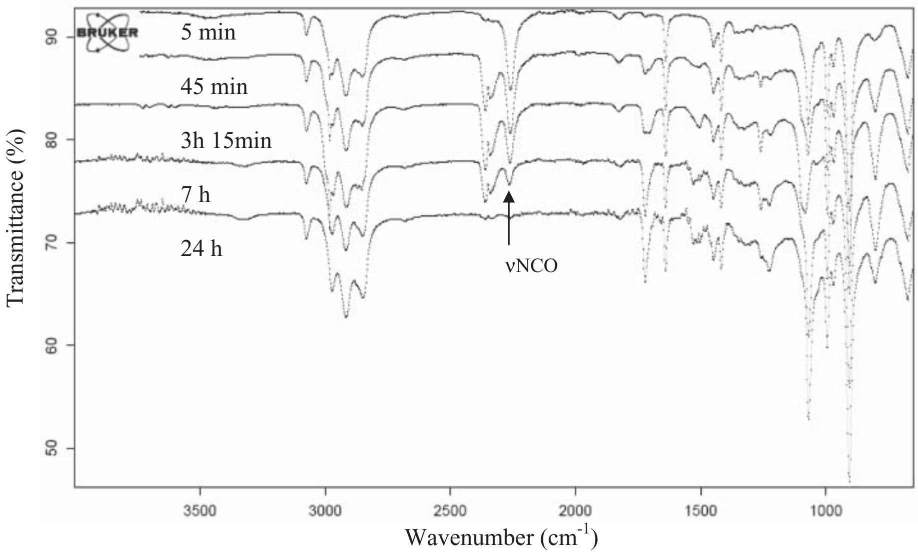

Fig. 6. Infrared monitoring of run 8 (T = 65°C, [DBTL] = 10^{-4} mol/L).

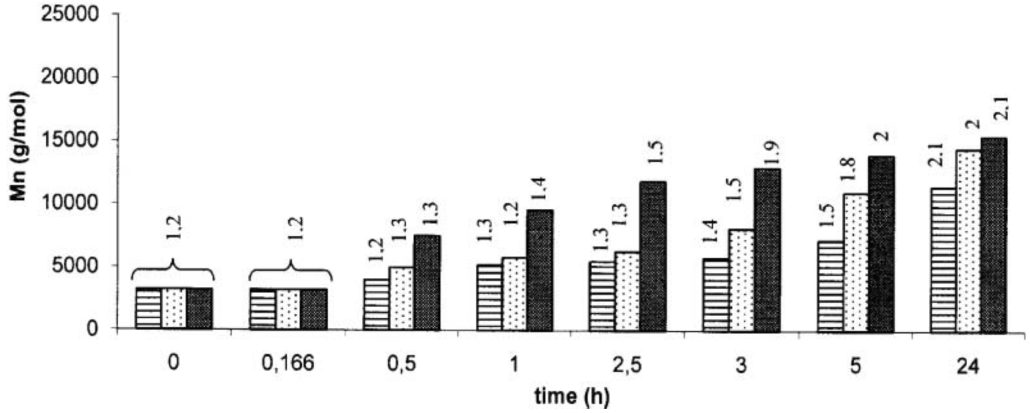

Fig. 7. Influence of catalyst concentration and time reaction on chain length at room temperature. for [DBTL] = 2.10^{-5} mol/L (▤), [DBTL] = 10^{-4} mol/L (▩), [DBTL] = 10^{-2} mol/L (■). The PDI values are given on the graph for the corresponding experiments.

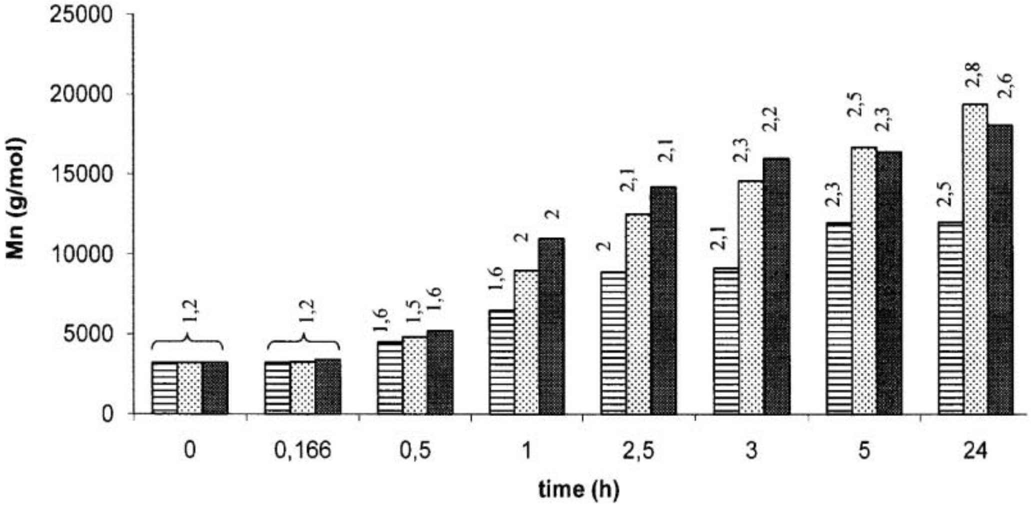

Fig. 8. Influence of catalyst concentration and time reaction on chain length at 65°C for [DBTL] = 2.10^{-5} mol/L(▤), [DBTL] = 10^{-4} mol/L (░), [DBTL] = 10^{-2} mol/L (■). The PDI values are given on the graph for the corresponding experiments.

from 1, the shorter the chains are. In these mild conditions, the best extension factor value is situated around six (based on $\overline{Mn}$ values) compare to three for a non catalyzed addition reaction.

In this work, we focused on the influence of the catalyst concentration on the final length of the chains after 24 h of reaction. In this aim, two studies (Figs. 7 and 8) were conducted in stoechiometric conditions at room temperature and 65°C. A preliminary kinetic monitoring by FTIR showed that all isocyanate functions were consumed after 24h of reaction at 65°C. It can be seen on Figure 6, that the specific isocyanate band at 2200 cm^{-1} disappears after 24 h of reaction.

In the presence of low DBTL concentration (2.10^{-5} mol/L), the maximum average molar mass molar (11500 g/mol) is obtained after 24 h of reaction at room temperature and after 5 h at 65°C (Figs. 7 and 8). For a higher DBTL concentration (10^{-2} mol/L), the maximum molecular weight achieved is limited to 15800 g/mol at room temperature while it is 18000 g/mol at 65°C. Whatever the DBTL concentrations used, the molar masses obtained at 65 °C after 24 h of reaction are higher than those obtained at room temperature. Indeed, for a DBTL concentration of 10^{-4} mol/L, the decrease of isocyanate groups is very fast, since 90% of the starting reagents were consumed after 3.5 h of reaction (Fig. 9). DBTL in a concentration of 10^{-4} mol/L seems to be optimal, since the kinetics of extension is not changed with a greater catalyst concentration.

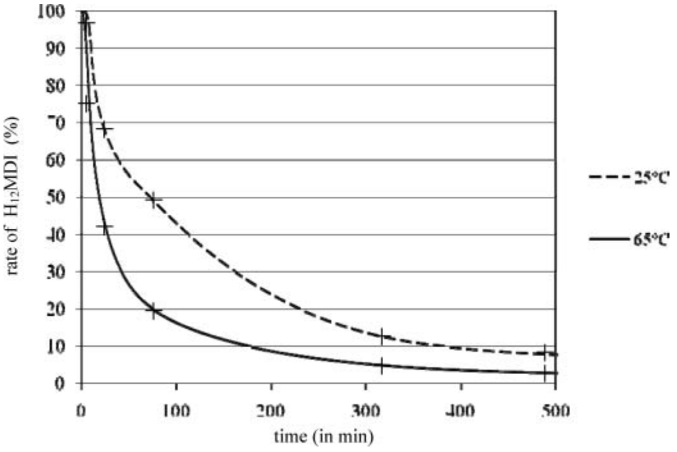

Fig. 9. $H_{12}MDI$ rate in the reaction medium for a reaction between HTPB and $H_{12}MDI$ for [DBTL] = 10^{-4}mol/L.

3.4 Glass Transition Properties of the Materials

Table 3 summarizes the T_g values of the extended materials obtained both from the anhydride and the diisocyanate route.

The relation between thermal properties and degree of polymerization of low molecular weight polymers has received considerable attention in the last few years. It is a common view that the T_g value must increase on increasing the molecular weight. This is due to the progressive gain

Table 3. Average molar mass and glass transition temperatures of extended oligomers by the anhydride and the diisocyanate routes

Run	$\overline{Mn}$	$\overline{Mw}$	*DPI*	T_g *(°C)*
HTPB	3200	5100	1,6	−20
3 (anhydride)	4100	8200	2	−21
4 (anhydride)	6700	12300	1,8	−21
9 (anhydride)	8000	12800	1,6	−22
10 (diisocyanate)	12200	34200	2,8	−6
11 (diisocyanate)	8100	16000	2	−14
12 (diisocyanate)	18000	50400	2,8	−1.5

of the cohesive state of the system because of the weaker mobility of the end units compare to those of the molecular backbone. This effect is observed when the end groups have chemical similarity to the repeating units. However, in the case of HTPB G2000®, the end groups are chemically different of the molecular backbone and the glass transition temperature of the oligomers is $-20°C$. This T_g, relatively high for an elastomeric polybutadiene, is due to the presence of hydrogen bonds occurring between the hydroxyl ends, in the bulk material.

The extension of HTPB by insertion of ester linkages does not modify the Tg of the materials meaning that the establishment of hydrogen bonds was not disturbed in the bulk material.

On the contrary, the behaviour of materials containing urethane linkages is strongly affected by the extension. Indeed, an increase in T_g is observed when the size of the oligomers increases (runs 10 to 12). This increase in T_g can be attributed to the strong hydrogen bonds established both between the C=O and the N-H groups of the urethane functions and the hydroxyl extremities. Another reason for the increase of T_g could be the rigidity of the methylene dicyclohexane rings brought by the diisocyanate links.

4 Conclusions

In this work, it was demonstrated that HTPB oligomers could be easily extended using difonctional reactive linkers such as succinic anhydride or methylenedicyclohexyl diisocyanate. The experimental conditions are chosen in order to allow the conservation of the hydroxyl extremities. Starting from 3200 g/mol oligomers (PS equivalent), the use of succinic anhydride in the presence of DMAP and DCC, at room temperature, allows the extension of the HTBP chains by a factor 3. The diisocyanate route allows the extension of the HTBP chains by a factor 5.4 when the reaction is performed at 65°C. The thermal properties study of the extended materials reveals that the choice of the linker between the HTPB blocks governs the T_g values. Indeed, glass transition temperature of materials extended with ester links are much lower than those of materials extended with carbamate links.

References

1. Pinazzi, C., Legeay, G., and Brosse, J.C. (1975) *Makromol. Chem.*, 5, 1307–1322.
2. Brosse, J.C., Legeay, G,. Lenain, J.C., Bonnier, M., and Pinazzi, C. (1978) *Makromol. Chem.*, 1, 79–85.
3. Legeay, G., and Brosse, J.C. (1976) *Makromol. Chem.*, 177, 2877–2896.
4. Pradel, J.L., and Bonnet, E. (2001) Techniques de l'Ingénieur. Oligomères hydroxytéléchéliques de butadiène PBHT AM3430.
5. Abadie, J.M., and Satibi, L. (1987) *Eur. Polym.*, 23, 423–431.
6. Jin, G.T., and Li, T.H. (1992) *J. Polym. Mater.*, 9(1), 49–54.
7. Szwarc, M. (1983) *Adc. Polym. Sci.*, 49, 171–177.
8. Schulz, D.N., Sanda, J.C., and Willoughby, B.G. (1981) ACS Symp. Series, 166(27), 427–440.
9. Sureshkumar, M.S., Bhuvaneswari, C.M., Kakade, S.D., and Gupta, M. (2008) *Polym. Adv. Tech.*, 19(2), 144–150.
10. Patri, M., Rath, S.K., and Suryavansi, U.G. (2006) *J. Appl. Polym. Sci.*, 99(3), 884–890.
11. Pasadena, CA (1980) California Institute of Technology, US 4,196,129.
12. Houston, TX (1999) Shell Oil Company, US 5, 925,724.
13. Sarkar, S., and Adhikari, B. (2001) *Polym. Degrad. Stab.*, 73, 169–175.
14. Desai, S., Thakore, I.M., Sarawade, B.D., and Devi, S. (2000) *Eur. Polym. J.*, 36, 711–725.
15. Sekkar, V., Ninan, K.N., Krishnamurty, V.N., and Jain, S.R. (2000) *Eur. Polym. J.*, 36, 2437–2448.
16. Banu, P., and Radhakrishnan, G. (2004) *Eur. Polym. J.*, 40, 1887–1894.
17. Thomas, V., Jabalayan, M. (2002) *Biomaterials*, 23, 273–82.
18. Coutinho, F.M.B., Delpech, M.C., Alves, T.L., and Ferreira, A.A. (2003) *Polym. Degrad. Stab.*, 81, 19–27.
19. Lemoine, M., Brachais, C.H., Boni, G., and Couvercelle, J.P. (2009) *ePolymers*, no. 032.
20. Chen, H.X., Sun, H.Y., and Zheng, M.S. (2006) *Huaxue Yu Nianhe*, 28(3), 200–202.
21. Kim, H.D., Kang, S.G., and Ha, C.S. (1992) *J. Appl. Polym. Sci.*, 46(8), 1339–1351.
22. Pham, Q.T. (1981) *Makromol. Chem.*, 182, 1167–1176.
23. Zhang, X., Zhang, W., Zhu, H., and Wang, C. (2008) International Annual Conference of ICT, 39th, p. 81/1–81/7.
24. Rauf, A., and Parveen, H. (2004) *Eur. J. Lipid Sci. Technol.*, 106, 97–100.
25. Hassner, A., and Alexanian, V. (1978) *Tet. Let.,* 46, 4475–4478.
26. Kojio, K., Mitsui, Y., and Furukawa, M. (2009) *Polymer*, 50(15), 3693–3697.
27. Meltzer, D.A. (2009) PCT Int. Appl., WO 2009079360.
28. Petrova, T., Manolova, N., Rashkov, I., Li, S., and Vert, M. (1998) *Polymer International*, 45, 419–426.